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# PATENT SPECIFICATION

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## (54) AMINE TERMINATED POLYURETHANE UREA POLYMERS CURED WITH EPOXIDES

(71) We, Witco CHEMICAL CORPORATION, a corporation organised and existing under the laws of the State of Delaware, United States of America, of 277 Park Avenue, New York, State of New York, 10017, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

"This invention relates to a curable polymer-forming composition which comprises an amine-terminated polyether-urethane-urea and an epoxide in one or more organic solvents". The epoxide is added to a solution of an amine terminated polyetherurethane-urea to produce a cured polyetherurethane-urea system from which coatings, films, or adhesives having improved hydrolytic resistance, and improved physical properties may be prepared.

The curing of a polyamide with an epoxide and vice-versa is well known in the art. 25 This technology is found in the patent literature such as for instance in U.S. 2,500,600 issued to Bradley on March 14, 1950; U.S. 2,829,984, issued to Yeager on April 8, 1958; U.S. 2,880,194, issued to Glasser on March 31, 1959; U.S. 3,374,186, issued to Steden et al on March 19 1968; and U.S. 3,496,138, issued to Sellers et al on February 17, 1970.

U.S. 3,510,439, issued to Kaltenbach on May 5, 1970, discloses a polyurethane prepolymer formed by the reaction between toluene diisocyanate and a polyalkylene ether or ester glycol and characterized by an isocyanate content of from 4-10%, condensed with a low molecular weight liquid epoxy resin, a solid primary diamine and a naphthenate, tallate, or octoate salt of manganese, zinc, iron or lead, cured by heating. U.S. 3,565,972, issued to Harris on February 23, 1971, discloses a high strength

structural adhesive formulation which may be employed in either a one part or multi-part composition. In both cases the formulation contains a polyurethane prepolymer formed by the reaction of TDI with a poly-alkylene ether glycol, a low molecular weight liquid epoxy resin derived from bisphenol A and epichlorohydrin, a latent solid primary diamine, and a small but effective amount of a Lewis acid-amine complex. 50 U.S. 3,384,679 issued to Stetz et al on May 21, 1968, discloses a product which is made by blending a thermoplastic polyester or polyetherurethane with a thermoplastic copolymer of bisphenol A and epichlorohydrin. 60 The polyurethanes disclosed in this patent are not amine terminated and they are made by blending the thermoplastic polyurethane with a thermoplastic copolymer of bisphenol A and epichlorohydrin. 65

None of the art known to us makes available the present two component system for making improved coatings, films, and adhesives.

According to the present invention, there 70 is provided a curable, polymer-forming composition which comprises an amine-terminated polyetherurethane-urea and epoxide in one or more organic solvents.

As specifically exemplified hereinafter 75 the present invention makes available compositions which may be used to produce e.g. films, coatings, and adhesives having improved properties.

Specifically this invention deals with iso-cyanate terminated polyurethane prepolymers chain-extended with an excess of diamine, which diamine is preferably admixture with a small amount of a mono-amine in one or more organic solvents such 80 as the known lacquer solvents, the solvent preferably containing a monohydric alcohol, and cured with an epoxide preferably a polyepoxide, just before using, as will be 85 more fully described hereinafter.

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The isocyanate terminated prepolymer is preferably prepared from a difunctional polyalkylene ether glycol and a diisocyanate. The glycol ether can suitably be poly-  
 5 (oxytetramethylene)glycol, poly(oxyethylene)glycol, poly(oxypropylene)glycol, and polyethers prepared from mixtures of epoxides, i.e. mixtures of two or more of ethylene oxide, propylene oxide, styrene oxide, and  
 10 epichlorohydrin, copolymers of the same and mixtures of any of the above. The isocyanate may be aliphatic, cycloaliphatic, or aromatic, such as hexamethylene diisocyanate, methylene bis(cyclohexyl isocyanate), and toluene diisocyanate, as known in the art. Such prepolymers appear throughout the patent literature, *vide supra*, and require no further discussion herein.

The prepolymer above is allowed to react  
 20 with excess diamine, preferably a cycloaliphatic diamine, with 3-aminomethyl-3,5,5-trimethyl cyclohexylamine, 1,8-diamino-p-methane, and hexahydropyrazine, being particularly preferred. Although other aliphatic branched or cyclic diamines may be employed, best results are obtained from the above cycloaliphatic diamines. Aromatic diamines are also operable in the present concept, but because of discoloration by the  
 25 aromatic moiety, they are not preferred. By "operable" is meant that the final films produced from the present two component solution have improved hydrolytic stability.

In the practice of the present invention,  
 30 the isocyanate terminated prepolymer is allowed to react with excess diamine to form the polyetherurethane-urea, by adding the prepolymer to a solution of diamine, in a solvent such as toluene, methyl ethyl  
 35 ketone, dimethylformamide, or other organic solvent, and preferably a conventional lacquer solvent, preferably containing an amount of C<sub>1</sub>-C<sub>5</sub> monohydric alcohol such as methanol, ethanol, isopropanol. The amount  
 40 of alcohol employed can be as little as 5% by weight or even less, and up to 100% of the solvent used, i.e. the complete solvent system can be a monohydric alcohol, and  
 45 preferably isopropanol because of its ready availability, low toxicity and ease of evaporation.

It is preferable, according to the present invention, to achieve the proper balanced polymer solution for making improved films  
 50 and coatings, for instance, that a monoamine is added with the excess diamine to react with the prepolymer, in amounts up to about 25% of the equivalents, based upon the total amine employed. The monoamine  
 55 is preferably an alkylamine such as methylamine, ethylamine, cyclohexylamine, diethylamine, and diisopropylamine, or an alkanolamine such as ethanolamine, diethanolamine, or isopropanolamine. Why the addition of a minor quantity of monoamine in

the preparation of the amine terminated polyetherurethane-urea is beneficial is not completely understood, but it is beneficial and as stated above, it represents a preferred embodiment.

According to the present invention, amine-terminated polyetherurethane-urea solutions of almost any viscosity can be employed, depending on the end use of the polymer and practical considerations. Good  
 70 results are obtained, for instance, from polyetherurethane-urea solutions having a viscosity in the range of about 7,000-15,000 cps at 20°C. for making films and coatings, and solutions of lower viscosity of as little 80 as about 200 cps at 20°C., or even lower, are operable, but not preferred. When making caulking compositions the viscosity can be 400,000 cps at 20°C. or even greater, as known in the art. It is preferred of course to employ the least possible solvent so that less solvent need be evaporated for curing.

The high molecular weight amine terminated polyetherurethane-urea in solution, advantageously is stable at ambient temperatures and may be stored until ready for use. Before use, this solution is treated with an epoxide such as the diglycidyl ether of p,p'-isopropylidenediphenol and the di-glycidyl ether of the corresponding sulfone,  
 90 or a polyepoxide of known phenol-formaldehyde resins; or 1,2,3-tris-(2,3-epoxy-propoxy, propane) thus chain-extending the amine terminated polyetherurethane-urea  
 95 and thereby increasing the molecular weight. Monoepoxides, such as butyl glycidyl ether for instance, can be employed in the present invention and offer an advantage in the preparation of lower molecular weight polymers, but because higher molecular  
 100 weight polymers are desired the di- and tri-epoxides, such as the triglycidyl ether of phenol-formaldehyde/resin, the diglycidyl ether of p,p'-isopropylidenediphenol and the tri-glycidyl ether of glycerol, *supra*, for  
 110 instance, are preferred. This reaction proceeds slowly at ambient temperatures and fairly rapidly at elevated temperatures. The resulting film or coating, for instance, is generally aged for several days to insure  
 115 adequate curing.

Although the present two-component composition is prepared in organic solvents and can be used as such to make for instance films, and coatings, the organic solvent solution may also be mixed and emulsified with water before use as known in the art.

The present invention also includes a two component pack for use in the preparation of a cured polymer by mixing together the two components of the pack, which pack comprises as a first component a solution of an amine-terminated polyetherurethane-urea in one or more organic  
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solvents and as a second component an epoxide.

The following examples illustrate specific embodiments of the present invention and 5 are not intended to be limiting. All examples may include in the formula, additives such as antioxidants and U.V. screening agents as known in the art, as determined by the artisan. Generally the addition 10 of these agents, as known in the art, is preferred. Proportions are on a weight /weight basis unless otherwise specified.

The present invention includes only poly-etherurethane-ureas and does not include 15 polyesters.

#### EXAMPLE 1

1000 parts of poly(1,2-oxypropylene)glycol having a hydroxyl number 140, are dehydrated 20 at 100°C. for 1 hour at 2 mm. Hg. and then allowed to react at about 100°C. for two hours with 380 parts of toluene diisocyanate (80% 2,4; 20% 2,6 isomer). The prepolymer has a free NCO value of 25 5.7. Enough toluene is added to make a solution containing about 75% prepolymer and 25% solvent. With good mixing this prepolymer solution is added to a solution of 3-aminomethyl-3,5,5-trimethyl cyclohexyl-30 amine and diethylamine in a 70-30 mixture of toluene and isopropanol. In terms of equivalents the amount of diamine is 110% and the monoamine is 5% of the available NCO. Reaction takes place to produce an 35 amine terminated polyurethane urea. The final solution has a total solids content of 35%. To 100 parts of this solution is added 0.95 parts of an epoxylated phenol formaldehyde resin with a functionality of 3.8, 40 representing about 110% of the available amine in terms of equivalents. A film is drawn on silicone paper and then cured using standard coating procedure. This film is aged for 3 to 6 days. The final film has 45 good U.V., and excellent hydrolytic stability, and good abrasion resistance and stress-strain properties.

#### EXAMPLE 2

50 1000 parts of poly(1,2-oxypropylene)-glycol, hydroxyl number 56, are dehydrated at 120°C. for one hour at 4 mm. Hg. and then allowed to react at 100°C. for 4 hours with 137 parts of toluene diisocyanate, to 55 yield a prepolymer having a free NCO value of 2.1. Toluene is added to make a solution containing 90% solids. With good mixing this prepolymer solution is added to a solution of excess 3-aminoethyl-3,5,5-trimethyl 60 cyclohexylamine and monobutylamine, in a solvent mixture of 90% isopropanol and 10% toluene. The diamine is 104% and the monoamine is 3% of the available NCO value in terms of equivalents. Reaction takes 65 place to form an amino terminated poly-

urethane urea. The final solution has a total solids content of 40%. To 100 parts of this solution is added 0.38 parts of epoxy resin of the p,p-isopropylidenediphenolepi-chlorohydrin type having an epoxy equivalent weight of about 190, representing 70 about 140% of the available amine in terms of equivalents. The cast film after drying and aging for 3 to 6 days had good U.V., and excellent hydrolytic stability and good 75 physical properties as in Example 1.

#### EXAMPLE 3

1000 parts of poly(oxytetramethylene)-glycol, hydroxyl number 140, are dehydrated 80 at 100°C. for 1 hour at 1 mm. Hg. and then allowed to react at 100°C. for two hours with 380 parts of toluene diisocyanate (65% 2,4; 35% 2,6-isomer). The prepolymer has a free NCO value of 5.6. Enough 85 toluene is added to make a 75% solution of the prepolymer. With good mixing this prepolymer solution is added to a solution of 1,8-diamino-p-methane and dibutylamine, in a 50-30-20 mixture of methyl ethyl 90 ketone, toluene, and isopropanol. The diamine is 108% and the monoamine is 4% of the available NCO value in terms of equivalents. Reaction takes place to form an amine terminated polyurethane urea. 95 The final solution has total solids of about 35%. To this solution is added a diglycidyl ether of p,p-isopropylidenediphenol having an epoxy equivalent of about 175 in an amount just equivalent to the available 100 amine groups. An excellent polymer resulted after evaporation of solvent, which has excellent hydrolytic stability, good physical properties and shows only slight discoloration after exposure in an Atlas Weatherometer, at 145°F., 65% relative humidity, for 200 hours. (ATLAS is a registered 105 Trade Mark).

#### EXAMPLE 4

110 1000 grams of poly(oxyethylene)glycol, hydroxyl number 140, are dehydrated at 110°C. for 2 hours at 10 mm. Hg. and then allowed to react for 2 hours at 100°C. with 450 grams diphenylmethane-4,4'-diisocyanate. The prepolymer has a free NCO value 115 of 3.2. Enough toluene is added to make a 90% solution of the prepolymer. With good mixing this prepolymer is added to a solution of 3-aminomethyl-3,5,5-trimethyl cyclohexylamine and ethanolamine in 10-90 mixture of toluene and isopropanol. The diamine is 104% and the monoamine is 3% of the available NCO value in terms of equivalents. Reaction takes place to form 120 an amine terminated polyurethane urea. Total solids are 40%. To 100 parts of this lacquer is added 0.55 grams of an epoxylated phenol-formaldehyde resin having an 125 epoxy functionality of 2.2, before applying 130

to a surface to impart a coating having excellent hydrolytic stability. The epoxy represent about 140% of the available amine in terms of equivalents.

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#### EXAMPLE 5

1000 parts of poly(1,2-oxypropylene)-glycol, hydroxyl number 112, are dehydrated at 120°C. for 1 hour at 1 mm. Hg. and then allowed to react at 100°C. for 5 hours with 518 parts of methylene-bis(cyclohexyl isocyanate). The prepolymer has a free NCO value of 5.4. Toluene is added to make a 75% solution 15 of prepolymer. With good mixing this prepolymer solution is added to a solution of 3-aminomethyl-3,5,5-trimethyl cyclohexylamine and diethylamine in a 50-50 mixture of toluene and isopropanol. The diamine is 20 106% and the monoamine is 3% of the available NCO value in terms of equivalents. Reaction takes place to form an amine terminated polyurethane urea. The final solution has a total solids of about 25 35%. To 100 parts of this solution is added 0.7 parts of a diglycidyl ether of p,p'-isopropylidenediphenol which has a functionality of about 2. The epoxy compound is equivalent to about 120% of the available 30 amine in terms of equivalents. A film is drawn on the silicone paper and then cured using standard coating procedure. After allowing to age for 3 to 6 days, the film exhibits excellent hydrolytic stability, resistance to ultraviolet light and excellent physical properties as in Example 1.

#### WHAT WE CLAIM IS:—

1. A curable, polymer-forming composition which comprises an amine-terminated polyetherurethane-urea and an epoxide in one or more organic solvents.
2. A composition as claimed in claim 1 wherein the amine-terminated polyetherurethane-urea has been prepared from an isocyanate-terminated polyurethane prepolymer derived from a difunctional polyalkylene ether glycol and a diisocyanate, the prepolymer being subsequently chain extended 45 with an excess of diamine.
3. A composition as claimed in claim 2 wherein the difunctional polyalkylene ether glycol is poly(oxytetramethylene) glycol, polyoxyethyleneglycol or polyoxypropylene-glycol.
4. A composition as claimed in claim 2 or claim 3 wherein the diisocyanate is hexamethylene diisocyanate, methylene bis(cyclohexyl isocyanate) or toluene diisocyanate.
5. A composition as claimed in any one of claims 2 to 4 wherein the diamine is a cycloaliphatic diamine.
6. A composition as claimed in claim 5 wherein the cycloaliphatic diamine is in admixture with a monoamine.

7. A composition as claimed in claim 6 wherein the monoamine is an alkylamine or an alkanolamine.

8. A composition as claimed in claim 7 wherein the alkylamine is methylamine, ethylamine, butylamine, cyclohexylamine, diethylamine, diisopropylamine or dibutylamine.

9. A composition as claimed in claim 7 wherein the alkanolamine is ethanolamine, diethanolamine or isopropanolamine.

10. A composition as claimed in any one of claims 5 to 9 wherein the cycloaliphatic diamine is 1,8-diamino-p-menthane, hexahydropyrazine or 3-aminoethyl-3,5,5-trimethylcyclohexylamine.

11. A composition as claimed in any preceding claim wherein the amine-terminated polyetherurethane-urea has been prepared in a solvent which serves also as the organic solvent in which, in the final composition, the amine-terminated polyetherurethane urea and the epoxide are contained.

12. A composition as claimed in any preceding claim wherein the epoxide is a di- or tri-epoxide.

13. A composition as claimed in claim 12 wherein the epoxide is a diglycidyl ether of p,p'-isopropylidenediphenol or of the corresponding sulfone; a triglycidyl ether of glycerol; 1,2,3-tris(2,3-epoxypropoxy)propane or a triglycidyl ether of a phenol-formaldehyde resin.

14. A composition as claimed in any preceding claim and including one or more of toluene, methyl ethyl ketone and dimethylformamide as organic solvent.

15. A composition as claimed in any preceding claim wherein the amine-terminated polyetherurethane-urea and the epoxide are contained in a solvent mixture which comprises one or more C<sub>1</sub> to C<sub>6</sub> monohydric alcohols.

16. A composition as claimed in claim 15 wherein the solvent mixture comprises one or more of methanol, ethanol and isopropanol.

17. A composition as claimed in claim 15 or claim 16 wherein the solvent mixture comprises one or more C<sub>1</sub> to C<sub>6</sub> monohydric alcohols in an amount of at least 5% by weight of the mixture.

18. A composition as claimed in claim 1 and substantially as hereinbefore described in any one of the foregoing specific Examples.

19. A method of curing an amine-terminated polyetherurethane-urea dissolved in one or more organic solvents which method comprises adding thereto an epoxide and effecting curing.

20. A polymer obtained as the cured product of a method as claimed in claim 19.

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21. A two component pack for use in the preparation of a cured polymer by mixing together the two components of the pack, which pack comprises as a first component a solution of an amine-terminated polyetherurethane-urea in one or more organic solvents and as a second component an epoxide.

22. A two component pack as claimed

in claim 21 wherein the said solution has 10 a viscosity of from 7000 to 15,000 c.p.s. at 20°C.

BOULT, WADE & TENNANT,  
Chartered Patent Agents,

34 Cursitor Street,  
London, EC4A 1PQ.

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